

Characteristics of Coal / Tire Coliquefaction

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ABSTRACT

Batchwise tests were carried out to investigate synergistic effects and mechanism of the Alaskan subbituminous coal and waste tire coliquefaction. Coliquefactions brought synergistic effects of 22.09% and 9.94% respectively compared to independent liquefactions of coal or tire only at 450 . By considering the free radical theory, coliquefaction models were developed with effects of not only tetralin but tire. When the models were simulated to fit test results, they represented results and Arrhenius theory successfully. According to models, the amount of tetralin required to liquefy unit mass of coal increased from 0.71 to 1.63 as the coliquefaction temperature increased from 370 to 450 . This indicated that more tetralin was required to lower the molecular weight of liquefied products at high temperature.

1. Introduction

The coal liquid is still not in use because of its high price compared to oil. One of main reasons that make the coal liquid expensive is the consumption of hydrogen. According to the free-radical theory, coal matrix is thermally cleaved at the first stage of liquefaction and free-radicals are formed. Then, the radicals are stabilized by hydrogen donored. Therefore, hydrogen is necessary for the liquefaction of coal and cheap methods to supply hydrogen have been searched.

On the other hand, waste plastics and tires of high hydrogen content have caused serious environmental problems recently. For the case of tire, more than

20 million waste tires were produced annually and 80 percent was reused in Korea. However, use of waste tire has been limited to low value grade yet. Therefore, the use of waste tire as a hydrogen-donor source will reduce the coal liquid price and solve the environmental problem as well.

Waste tire containing high hydrogen($H/C \approx 1.2$) easily donates hydrogen during thermal cracking and can be used for coal liquefaction[6]. Orr[2], Liu[7] reported that coal / tire coliquefaction even gave synergistic effects. During the last 10 years, lots of coliquefaction tests with coal and tire have been conducted without verifying functions of each component[9,10]. Furthermore, investigations on either kinetics or synergistic mechanisms are rare.

In these respects, coal / tire coliquefaction tests were conducted to investigate synergistic effects by changing compositions, the amount of tetralin, and reaction temperature. Also, the coliquefaction model which satisfied the free-radical theory was developed and simulated to represent experimental results. Furthermore, coliquefaction effects were verified by measuring molecular weights and heating values of product liquid for various conditions.

2. Experimental

2.1. Materials

Ground Alaskan subbituminous coal(-200 mesh) and waste tire(-40 mesh) were used for coliquefaction tests. Those were stored under nitrogen gas to avoid oxidation prior to use. Proximate and elemental analyses of above materials are listed in Table 1. As a hydrogen donor solvent, tetralin (tetrahydronaphthalene, EP grade, Yakuri Chemical Co.) was employed. And, THF(tetrahydrofuran, EP grade, Duksan Chemical Co.) was employed as an extractant.

2.2. Experimental apparatus and procedure

Coliquefaction tests were conducted by using a tubing-bomb reactor(inside volume 50ml). The reactor was submerged in preheated fluidized bath(350 - 450) and vibrated vertically(200rpm) for a definite residence time(0 - 60min)

For tests, the mixture of coal and waste tire (total 4g) was slurried in tetralin (0 - 8ml). The slurry was injected in the reactor for tests.

2.3. Product analysis

After definite time of reactions, the tubing-bomb reactor was cooled down for 5 minutes in air and cold water. Then, the product was taken out to the thimble filter and oil was extracted in the Soxhlet apparatus by THF. The THF insoluble material was vacuum dried overnight and the conversion was calculated by the following equation

$$\text{Conversion} = \frac{(\text{Coal} + \text{Tire})_{\text{dry}} - (\text{THF insoluble})}{(\text{Coal} + \text{Tire})_{\text{daf}}}$$

The accuracy of $\pm 2\%$ could be maintained through reproducibility tests.

Tetralin is converted to naphthalene by donating hydrogen to free-radicals during coliquefaction processes. Therefore, conversion of tetralin to naphthalene could be measured by gas chromatography (Hewlett-Packard 4890A). For analyses, a capillary column (HP series 5301 m) was employed and a thermal conductivity detector was used.

Also, average molecular weights of liquid products were measured by GPC. The analyzer employed was HPLC (Shimadzu Model 13-A) with Shim-Pack CLCDS (4.6 \times 150) columns. As a detector, UV spectrophotometric detector (wave length 254nm) was used. The oven temperature was maintained as 40 °C. The amount of feed was 0.21 L and the concentration of injection was maintained as 0.5%

Finally, heating values of liquid products could be measured by the differential scanning calorimeter (TA Instrument, DSC 20/0)

3. Results and Discussions

3.1. Synergistic effects by coal / tire coliquefactions

By changing the compositions of coal / tire mixture and amounts of tetralin(0 - 8ml), coliquefaction tests were conducted at various temperatures (370 - 450).

According to results(Fig. 1) at 370 , the conversion increased(10 - 20%) when the portion of tire in mixtures was less than 50%. However, the conversion did not change significantly with increase of tetralin when the tire content was 66.66%. The same conversion of 56% could be obtained when the tire content was 66.66% without tetralin and when the tire content was 50% with 5ml of tetralin. This indicated the function of tire as a hydrogen donor solvent. Furthermore, higher conversion of 13% compared to the proportional yield could be achieved when the tire content was 66.66% without tetralin. This showed the synergistic effect of coliquefactions.

Test results at 410 (Fig. 2) showed that synergistic effects of 7 to 13% appeared only when insufficient amount of tetralin(< 2ml) was added. Therefore, tire was believed to donor hydrogen when the amount of tetralin was not enough. When sufficient amount of tetralin was added, it functioned as a hydrogen donor solvent.

At 450 , high synergistic effects(12 - 16%) could be achieved when 2 or 4ml of tetralin was added(Fig. 3). Especially, high yield of 80% could be obtained when 8ml of tetralin was added. Increase of tetralin was believed to prevent cocking of coal. Therefore, hydrogen from tetralin and tire could be used to liquefy coal at 450 .

Fig. 4 shows the effects of tetralin amount on conversion at 370 . During coliquefactions, the addition of tetralin enhanced conversions by 4 to 13%. However, the amount of tetralin had little effects on conversions when the amount of tetralin was more than 2ml. At 410 , effects of tetralin was severe(Fig. 5). Increase of tetralin from 0 to 4ml enhanced conversions about 30%(coal : tire = 2 : 1). This proved the function of tire as a hydrogen donor solvent. Furthermore, the function of tetralin was improved as the portion of tire in mixtures decreased. Considering that more than 4ml of tetralin did not influence of conversions, 4ml of tetralin appeared as the optimum amount at 410

Results of 450 (Fig. 6) showed that conversions increased with the amount of tetralin especially when the portion of coal in mixtures increased.

3. 2. Coliquefaction mechanism and kinetics

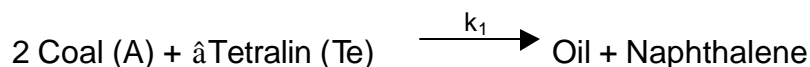
According to the free radical theory, free radicals formed from coal is stabilized by hydrogen[11]. Therefore, tetralin as a hydrogen donor solvent is converted to naphthalene by donating hydrogen to free radicals and this phenomenon can be detected by GC analysis.

The GC analysis showed that the liquefaction of tire only was independent of tetralin because tetralin was not converted to naphthalene under this condition. This is the same result with those by Lue[12] and Sharma et. al [13]. This is the important factor in investigating the coliquefaction mechanism.

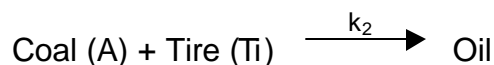
The conversions of tetralin during coliquefactions(coal : tire = 1 : 1) were measured for various temperature and compositions(Fig. 7). These results were used to simulate kinetic models.

To predict experimental results, kinetic models satisfying the free radical theory were developed. In models, THF soluble material was defined as oil and three steps were proposed as follows.

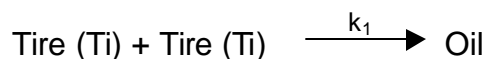
Model 1: Coal liquefaction by tetralin



Model 2: Coal liquefaction by tire



Model 3: Thermal decomposition of tire



Following rate equations were derived from above three models.

$$-r_c = -\frac{dC_c}{dt} = k_1 C_c^2 C_{Te} + k_2 C_c C_{Ti}$$

$$-r_{Ti} = \frac{dC_{Ti}}{dt} = k_3 C_{Ti}^2 + k_2 C_c C_{Ti}$$

$$-r_{Te} = -\frac{dC_{Te}}{dt} = \hat{a} k_1 C_c^2 C_{Te}$$

Where

C_c : concentration of coal [g/l]

C_{Te} : concentration of tetralin [g/l]

C_{Ti} : concentration of tire [g/l]

Above equations were integrated and simulated by the Marquardt method to fit experimental data. The results for various coliquefaction temperatures were shown in Fig 8, 9, 10 and 11. Also, rate constants together with corresponding frequency factors and activation energies were calculated and listed in Table 2 and 3. As shown in Fig 12, simulated models represented experimental results very successfully with the correlation coefficient of 0.99

The amount of tetralin(\hat{a}) needed to convert unit mass of coal into oil increased with temperature(Table 2). Furthermore, GPC analyses showed that average molecular weights of produced oil decreased at high temperature(370 , M.W. 438~463, 410 : 330~347, 450 : 125~184). This implies more hydrogen from tetralin is needed to lower the molecular weight of oil at high temperature.

Also, heating values of oil produced at 450 were measured by DSC. At 450 , the synergistic effect was greater than low temperature and measured heating values were listed in Table 4. According to Table 4, heating values of oil increased with tetralin addition. Depending on compositions, heating values of 44 to 52J/g were enhanced by increasing the amount of tetralin from 0 to 8ml. On the other hand, the heating value of oil formed from coal / tire mixture was found much higher than that from coal or tire only. Especially, this phenomenon

was severe when tetralin was not added. It is thought that tire enhances the heating value of oil during coliquefactions.

4. Conclusions

In this study, synergistic effects and kinetic mechanism were investigated by conducting coliquefaction tests with Alaskan subbituminous coal and waste tire. Tests were carried out for various compositions, temperatures, residence times and tetralin additions with results as follows.

- 1) Coliquefaction tests resulted in synergistic effects of 22 and 10% compared to the coal or tire liquefaction respectively at 450 . Especially, the synergistic effect of 16% could be achieved with the mixture (coal : tire = 1 : 1).
- 2) Coliquefaction models were developed to describe mechanisms. The models represented experimental results successfully and responded with Arrhenius' theory as well. Also, according to calculated models, the amount of tetralin for the conversion of unit mass of coal increased from 0.71 to 1.63 as temperature changed from 370 to 450
- 3) Average molecular weights of produced oil decreased from 438 ~ 463 to 125~184 as temperature changed from 370 to 450 . Also, it was found that the donorability of tetralin to free radicals increased and lowered molecular weights of oil at elevated temperatures.
- 4) Additions of tetralin and tire for coal liquefactions enhanced the heating values of oil from 38 to 141 J/g at 450 .

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Table 1. Proximate and elemental analysis of coal and tire

	Coal (wt%)	Tire (wt%)
F.C (as received)	36.91	23.40
H ₂ O (as received)	12.10	0.41
V.M (as received)	43.07	72.19
ASH (as received)	7.92	4.00
C (dmmf)	59.50	81.10
H (dmmf)	4.89	8.17
N (dmmf)	0.79	2.38
O (dmmf)	34.69	6.92
S (dmmf)	0.13	1.43

Table 2. Coliquefaction rate constants at different coliquefaction temperatures

rxn.temp.	370	410	430	450
k_1 [l ² ·g ⁻² ·min ⁻¹]	0.03315	0.3842	0.04159	0.04847
k_2 [l·g ⁻¹ ·min ⁻¹]	0.02014	0.02433	0.02901	0.03180
k_3 [l·g ⁻¹ ·min ⁻¹]	0.02269	0.02311	0.02375	0.02431
\hat{a}	0.70695	0.89569	10.0521	1.62770

Table 3. Frequency factors and activation energies of coliquefaction rate constants

rate constant	k_1	k_2	k_3
frequency factor (k_0)	0.84846 [l ² · g ⁻² · min ⁻¹]	0.28869 [l ² · g ⁻² · min ⁻¹]	0.04164 [l ² · g ⁻² · min ⁻¹]
activation energy (E)	17.43847 [KJ · mol ⁻¹]	22.50496 [KJ · mol ⁻¹]	3.27654 [KJ · mol ⁻¹]

Table 4. Heating values of liquid products

Coal:Tire				
Tetralin(ml)		1 : 0	1 : 1	0 : 1
450	0	38.2	89.1	51.9
	4	46.0	85.7	73.1
	8	76.6	141.6	95.4

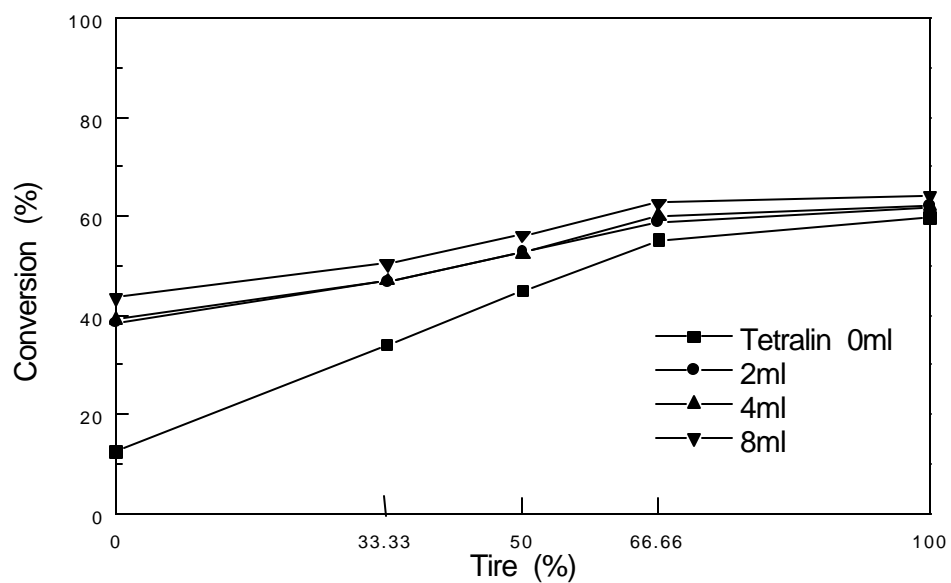


Fig. 1. Effects of tire contents on coliquefaction at 370 (reaction time : 30 min.)

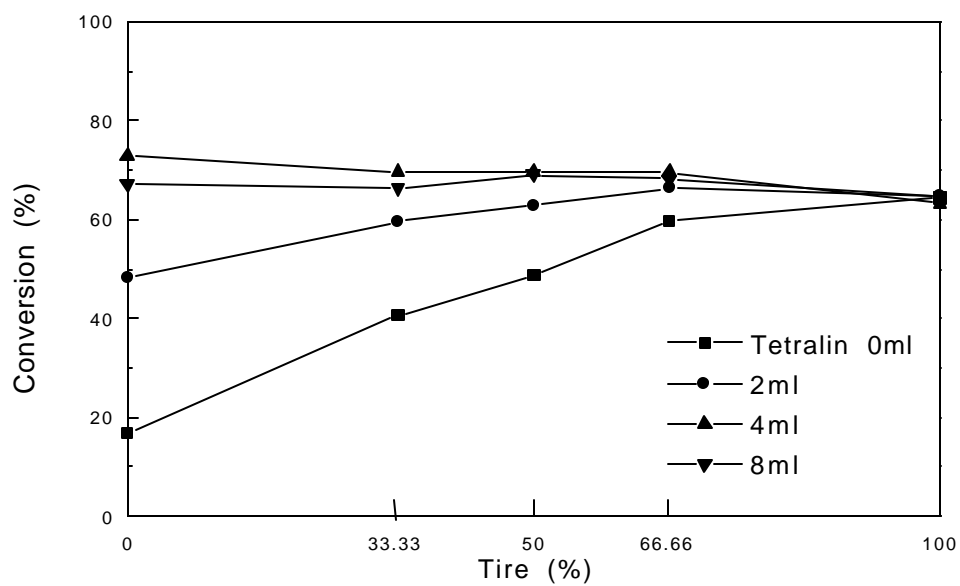


Fig. 2. Effects of tire contents on coliquefaction at 410 (reaction time : 30 min.)

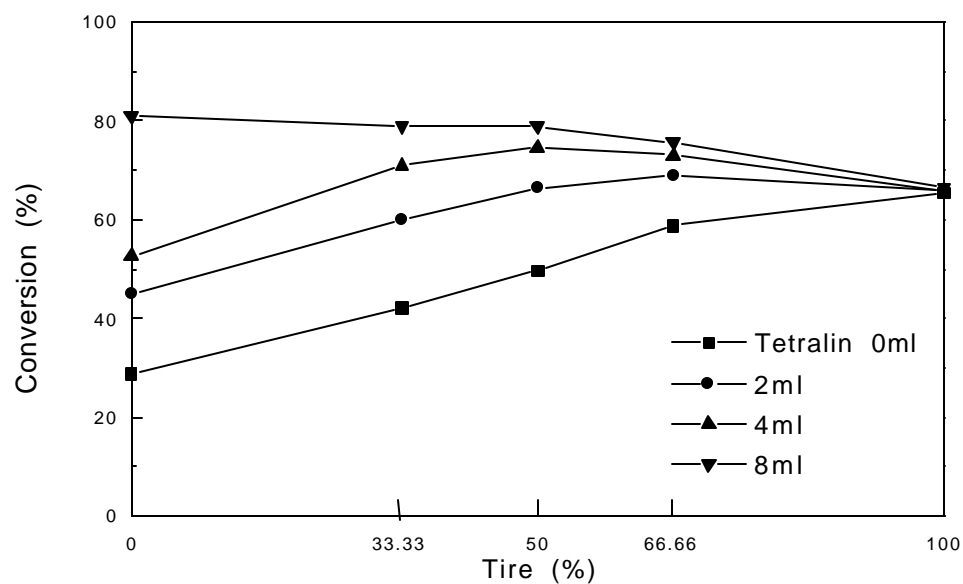


Fig. 3. Effects of tire contents on coliquefaction at 450 (reaction time : 30 min.)

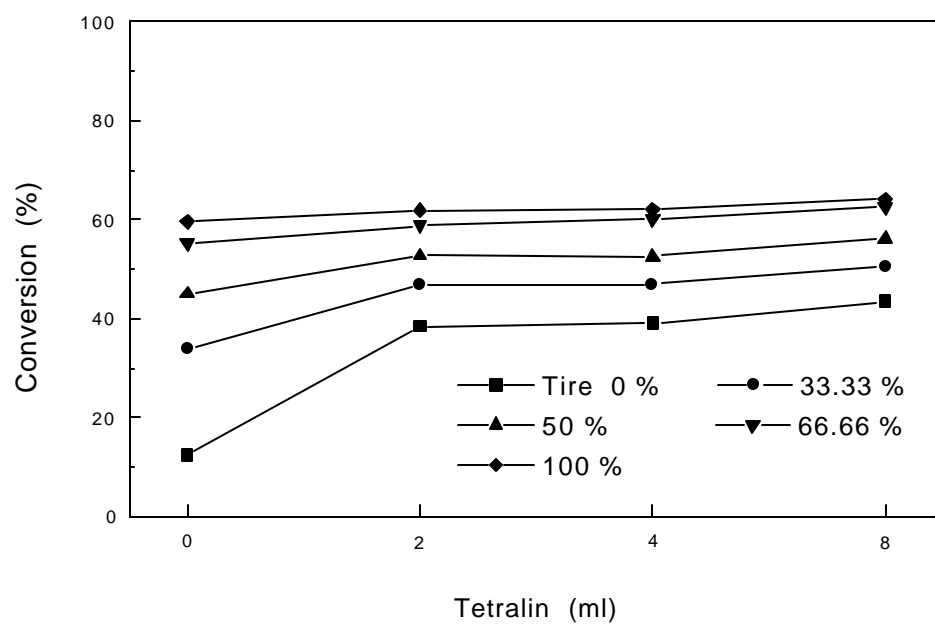


Fig. 4. Effects of tire contents on coliquefaction at 370 (t=30min., coal+tire=4g)

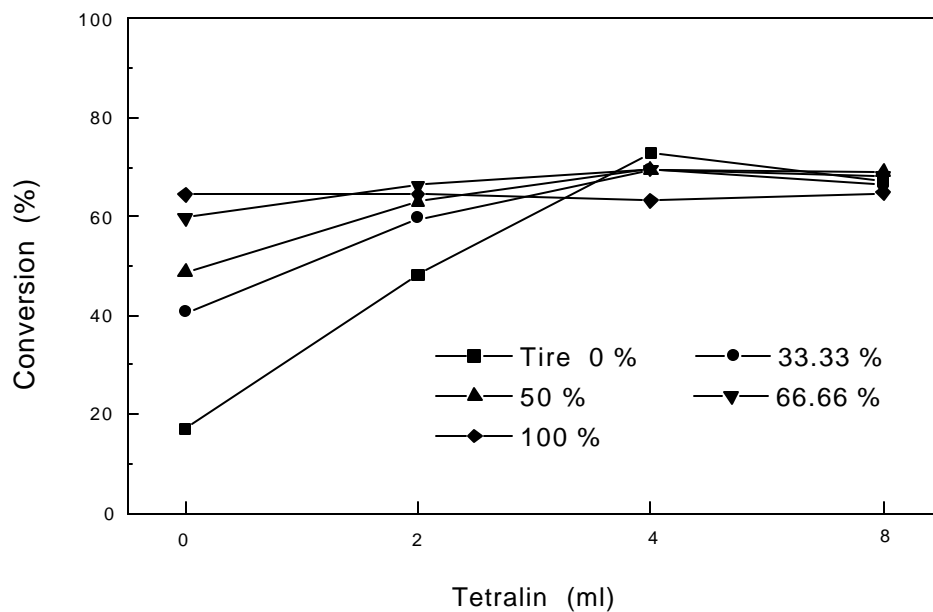


Fig. 5. Effects of tire contents on coliquefaction at 410 (t=30min., coal+tire=4g)

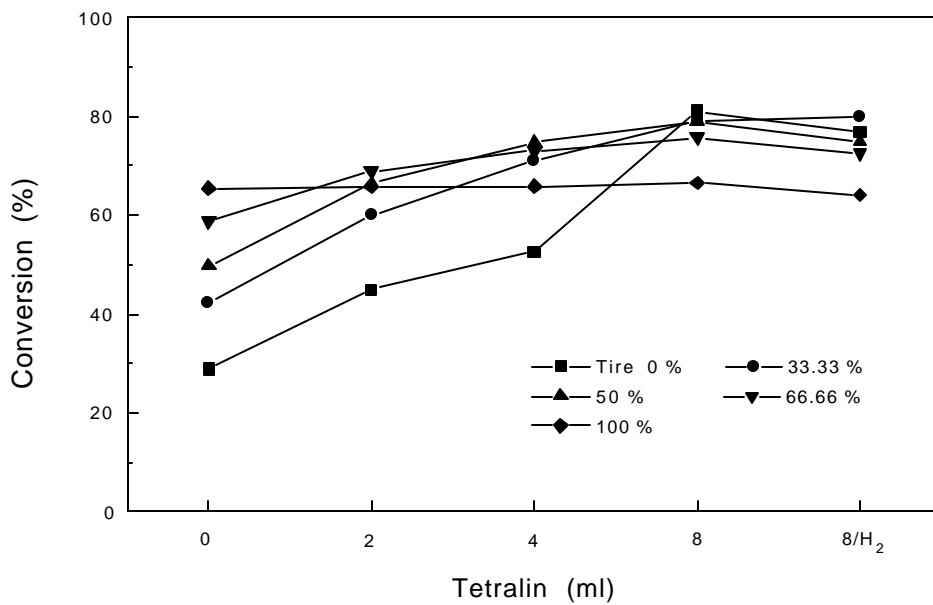


Fig. 6. Effects of tire contents on coliquefaction at 450 (t=30min., coal+tire=4g)

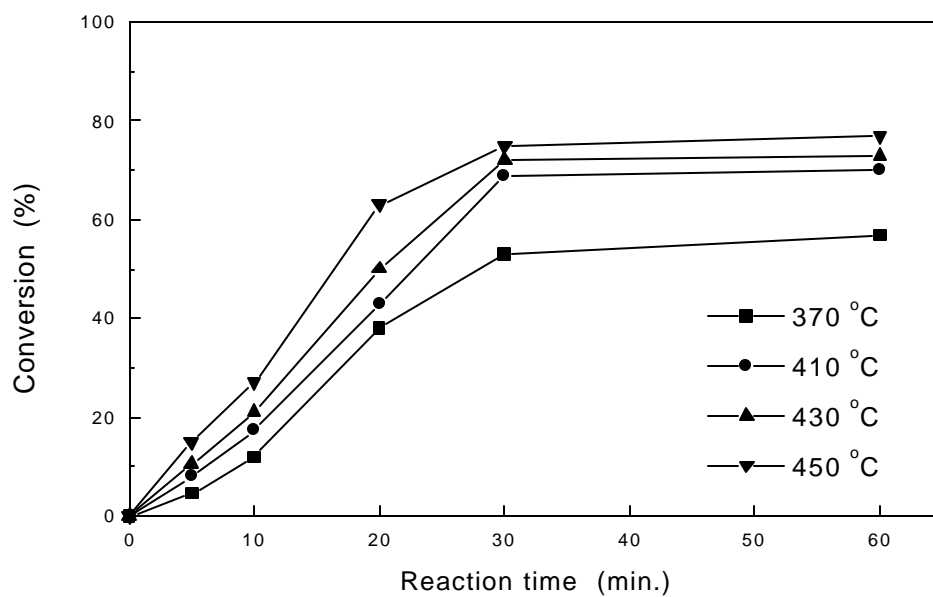


Fig. 7. Tetralin conversion to naphthalene during coal/tire coliquefaction (coal:tire=1:1, tetralin : 4ml)

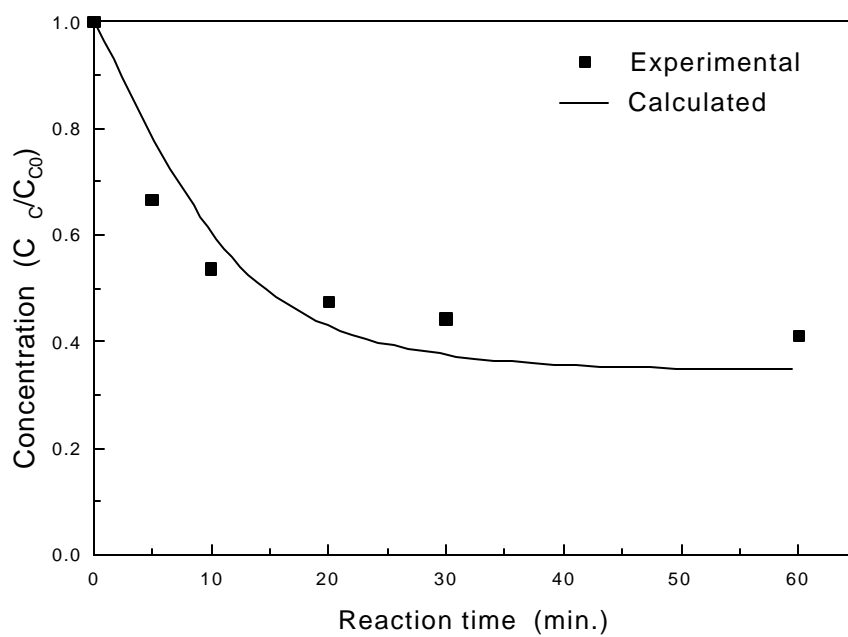
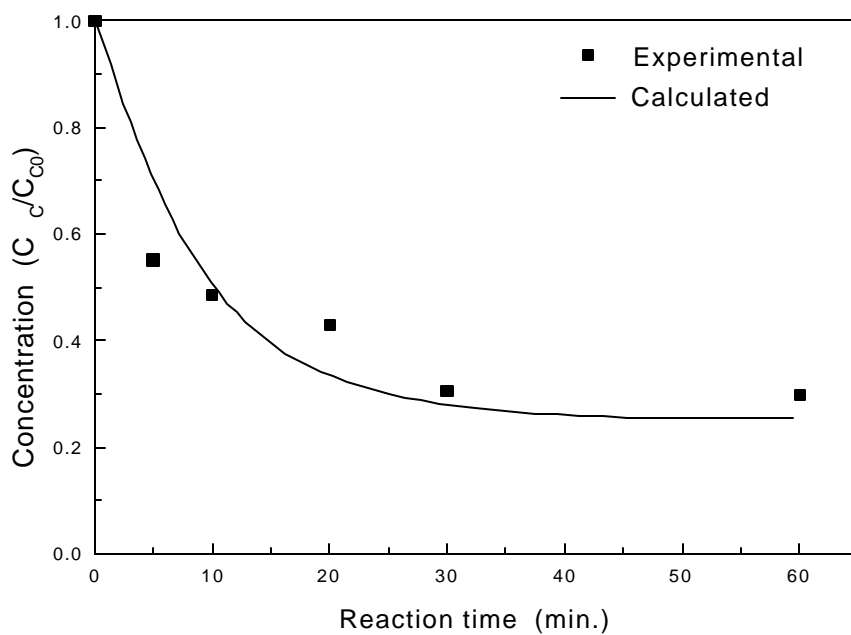
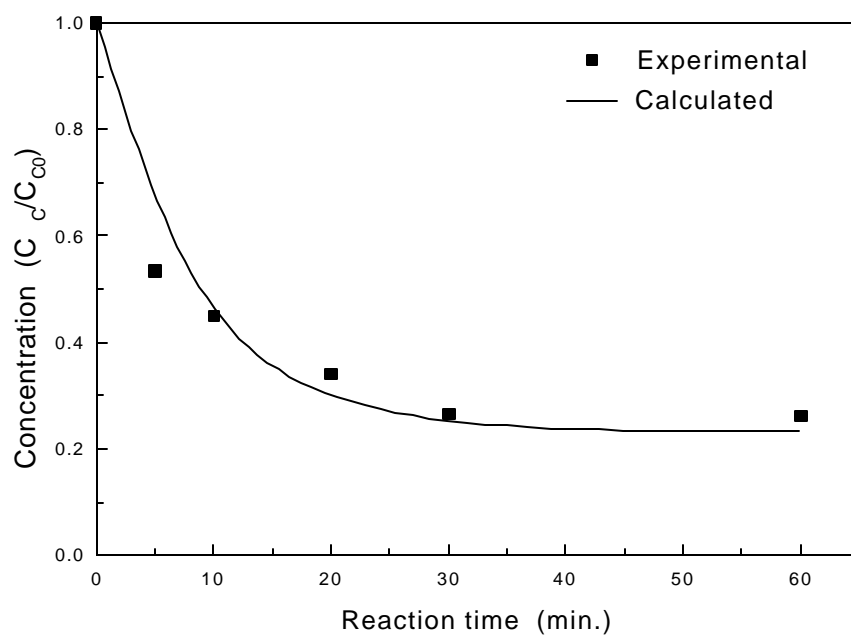


Fig. 8. Kinetic results of coliquefactions at 370 (coal:tire=1:1, tetralin : 4ml)



**Fig. 9. Kinetic results of coliquefactions at 410
(coal:tire=1:1, tetralin : 4ml)**



**Fig. 10. Kinetic results of coliquefactions at 430
(coal:tire=1:1, tetralin : 4ml)**

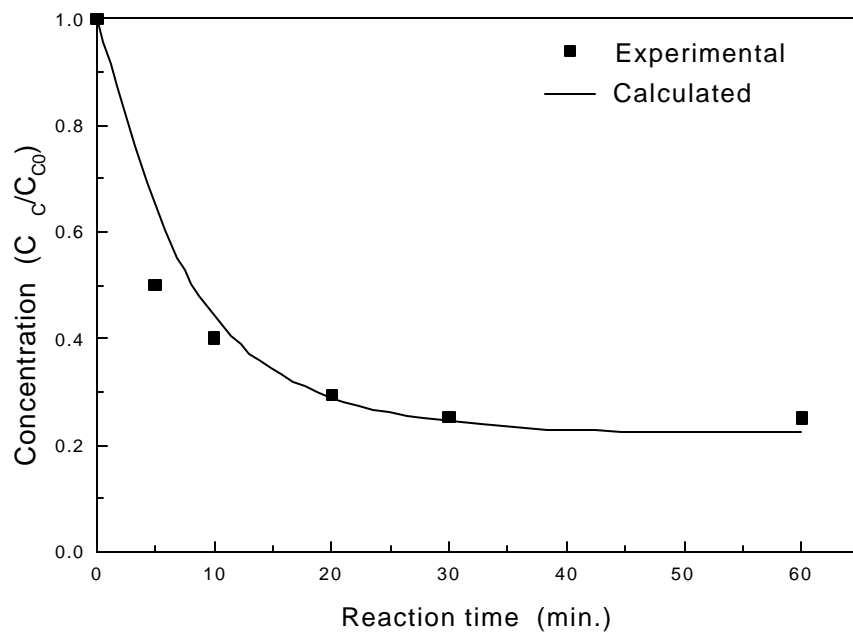


Fig. 11. Kinetic results of coliquefactions at 450 (coal:tire=1:1, tetralin : 4ml)

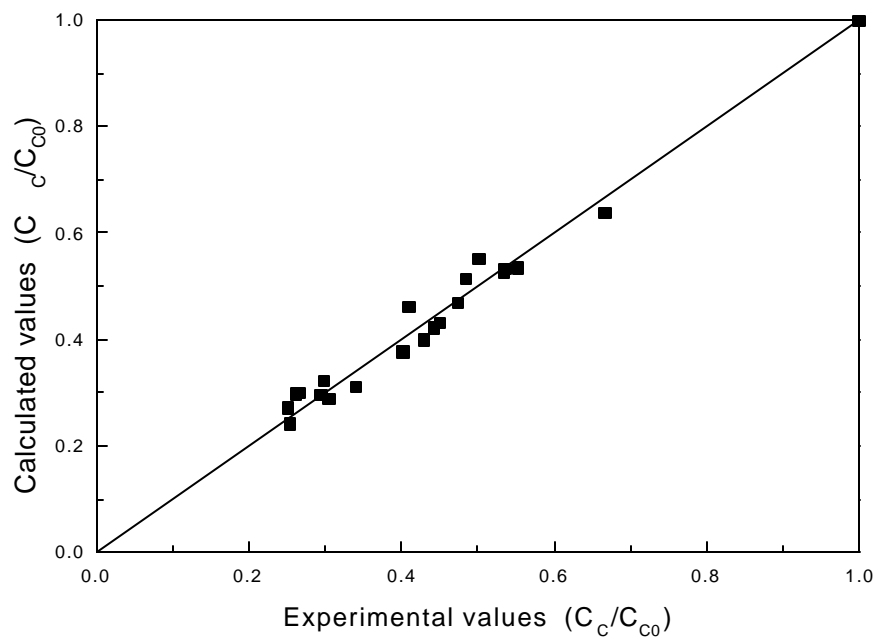


Fig. 12. Correlations between calculated and experimental conversions of coliquefaction